

HIGH PERFORMANCE SOFCs OPERATING AT TEMPERATURES BELOW 700 °C

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ABSTRACT

Interest in solid oxide fuel cells (SOFCs) capable of reduced temperatures operation has led to a number of innovations in the field of solid state ionics. The capability to fabricate electrode supported structures having thin electrolytes in the range of 5 to 40 μm has been demonstrated by a number of groups worldwide, as well as reports of good performance at intermediate temperatures. It is not yet clear how much the operating temperature can be dropped before electrolyte and electrode kinetic limitations reduce performance to unacceptably low levels. It is clear that yttria stabilized zirconia electrolyte is not suited to operating temperatures below 700 °C. However, alternative electrolyte and electrode materials are available that demonstrate excellent levels of performance at temperatures as low as 600 °C. Furthermore, the ability to fabricate both cathode-supported and anode-supported thin-film structures allows for great flexibility in the design of new SOFCs.

INTRODUCTION

Solid oxide fuel cells based on yttria stabilized zirconia electrolyte (YSZ) have been developed for operation in the temperature range of 950 to 1000 °C. Advantages of high temperature operation include internal reforming of fuels such as natural gas, and high quality waste heat. Conversely, reduction of the SOFC operating temperature by 200 °C or more broadens materials choices for the SOFC power plant and may lower manufacturing costs. Over the past few years various groups in the SOFC community have developed fuel cells capable of operating at significantly lower temperatures (1,2,3) of 700 to 800 °C. The motivation for these efforts includes the possibility of using metallic interconnects and greater flexibility in cell design. However, electrolyte conductivity and electrode kinetics drop significantly with lowered operating temperature. Ohmic losses across the electrolyte can be minimized in two ways: the use of higher conductivity materials and/or through the use of thin electrolyte membranes. The use of thin electrolyte membranes can be achieved in a number of ways and is relatively straightforward, whereas the use of alternative electrolytes introduces uncertainties in terms of long-term stability and materials compatibility. Electrode kinetics can be improved by increasing the electronic/ionic and catalytic properties of the fuel and air electrodes. This can be achieved through the use of new materials and

electrode structures that would not be stable at temperatures of 950 to 1000 °C. The group at LBNL has explored both thin electrolyte membranes as well as alternate solid electrolyte materials. In some cases the use of alternative electrolytes has broadened the choice of catalytic electrodes.

EXPERIMENTAL

Ytria (8 mol%) stabilized zirconia powders were obtained from Tosoh Co., Ltd. Scandia stabilized zirconia (SSZ), and samaria and gadolinia doped ceria electrolytes were prepared by the glycine-nitrate combustion synthesis process (4). Nickel oxide, NiO, was obtained from J.T. Baker Inc. In order to increase the porosity of the electrode substrate, a pore former (corn starch) was used in the electrode formulation. Air electrode materials $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) and $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.98}\text{Ni}_{0.02}\text{O}_3$ (LSCN) powders were also prepared by the glycine nitrate process using a glycine to nitrate ratio of 0.50.

Anode supported or cathode supported thin-film structures are fabricated through colloidal deposition techniques. For an anode-supported structure, NiO is mixed with the appropriate electrolyte and milled to a homogeneous powder.

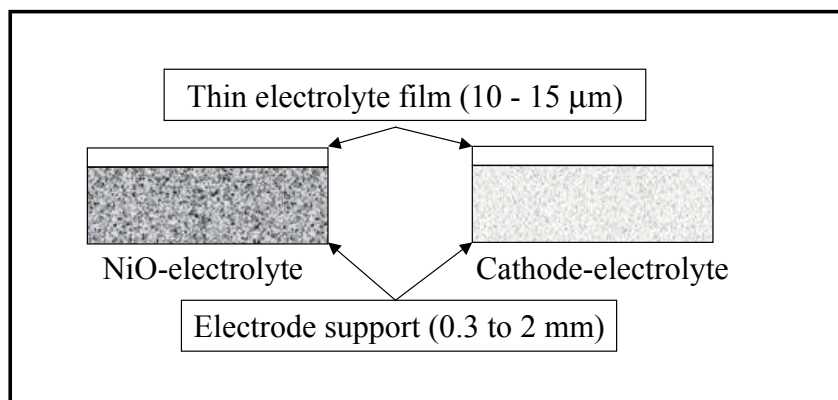


Figure 1. Possible configurations for co-fired thin-film bilayers.

Similarly, cathode-supported structures are made from mixtures of catalytic material and the electrolyte. The choice of anode-supported or cathode-supported structures is driven both by SOFC design and materials compatibility at the sintering temperature of the thin electrolyte film. The electrodes are die-pressed at low pressure to 300 to 2000 μm thickness and bisque fired to allow handling. The electrodes are then coated with a colloidal dispersion of the electrolyte. The group at LBNL has achieved dense, pinhole-free coatings with a variety of techniques including dip-coating, spray-coating, and electrophoretic deposition. The choice of configuration, either anode-supported or cathode-supported, is driven by cell design and/or materials compatibility issues at the sintering temperature of the bilayer structure. For the case of planar SOFCs based on zirconia electrolyte, co-firing of a NiO-YSZ substrate with a thin YSZ film is a relatively straightforward procedure due to the lack of reactivity at the electrolyte/electrode interface at the sintering temperature of 1300 to 1500 °C (depending on electrolyte material). The bilayer structures are typically sintered for 4 hours before cooling to room temperature. The counter electrode is then applied to the bilayer and

fired at 1000 to 1100 °C for 4 hours. Platinum screens are then bonded to the electrode faces of the fuel cell with Pt paste at 950 °C and Pt leads are spot welded to these current collectors.

Thin-film fuel cells are sealed to alumina tubes with Aremco cement. A type K thermocouple is fixed at the surface of the cathode current collector to obtain accurate cell temperature during operation. Hydrogen gas saturated with water vapor at room temperature is used as fuel for the anode; air is used as the oxidant at the cathode.

For a tubular SOFC where an air electrode supported film might be desired (YSZ on LSM support), care must be taken to avoid formation of lanthanum zirconate during co-firing. Our group has been successful at fabricating both anode supported and cathode supported structures that exhibit high power densities at reduced temperatures. Key to obtaining dense pinhole-free electrolyte layers is careful matching of electrode and electrolyte shrinkage during sintering. Thin-film SOFCs based on yttria-stabilized zirconia (YSZ), scandia-stabilized zirconia (SSZ), samaria-doped ceria (CSO), and many others have been prepared.

DISCUSSION

In Figure 2, the calculated ionic resistance for 10 μm films of several solid electrolytes are shown. Above 700 °C the areas specific resistance of a thin YSZ film is almost negligible. However, at temperatures approaching 600 °C the ionic resistivity of YSZ increases to where it limits fuel cell performance.

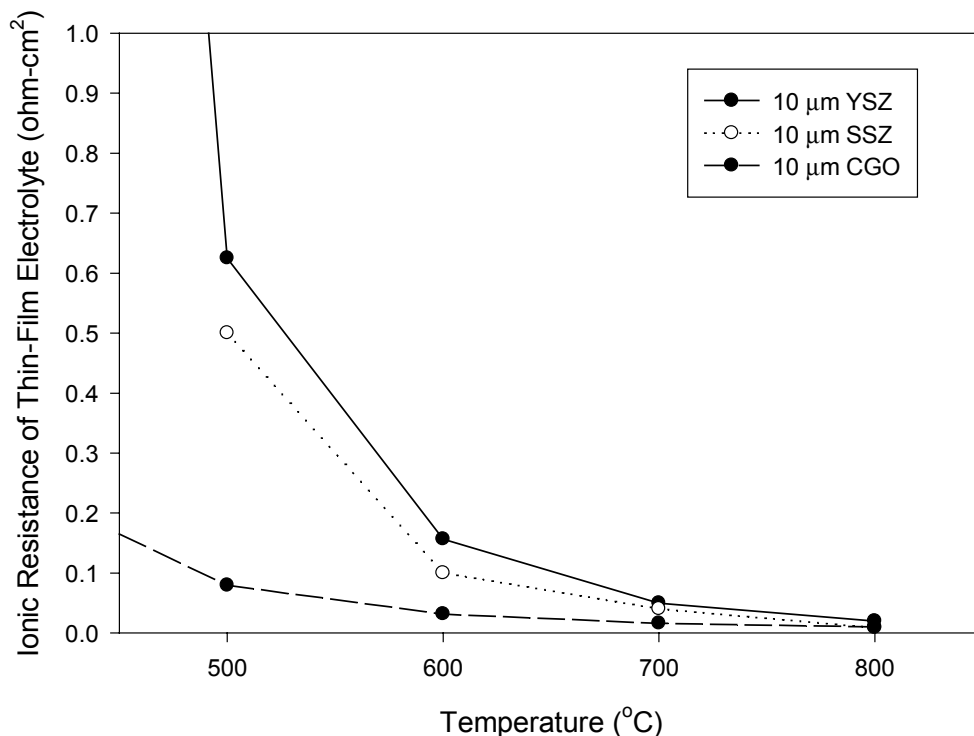


Figure 2. Ionic Resistance of 10 μm Electrolyte Films

Anode-supported Cells

In the temperature range of 600 to 700 °C scandia doped zirconia (SSZ) offers significantly higher conductivity than YSZ. The high cost of scandia is compensated somewhat by the use of thin electrolyte films. In Figure 3, a cross section of a SSZ thin-film cell fabricated in our laboratory is shown. Although the higher conductivity of the scandia stabilized electrolyte implies better performance of SSZ based thin-film cells compared to YSZ cells, this has not been observed. In Figure 4 and Figure 5, the current-voltage and power density of the LBNL SSZ thin-film cells at 800 °C is shown. The peak power for these cells, approximately 700 mW/cm² is lower than we typically see for YSZ cells; in fact performance of up to 2 W/cm² has been observed for thin-film YSZ cells (2). The lack of performance enhancement of the SSZ cells may be due to poor electrode microstructure; SEM cross-sections (Figure 3) show a relatively dense microstructure for the LSM-SSZ cathode.

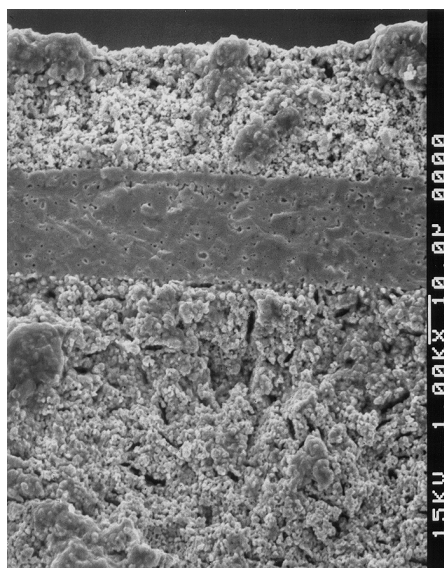


Figure 3. SEM of fracture section of NiO-SSZ/SSZ/LSM-SSZ cell

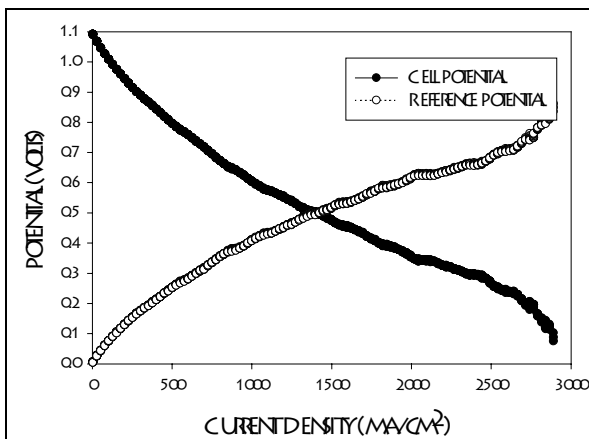


Figure 4. Performance of (H₂/H₂O)NiO-SSZ/SSZ/LSM-SSZ thin-film cell at 800 °C.

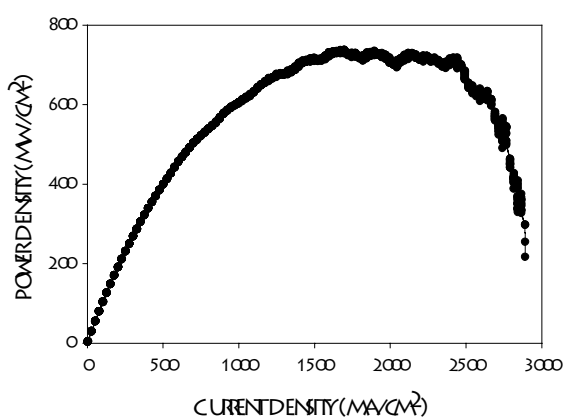


Figure 5. Power density of SSZ based thin-film cell at 800 °C.

Although thin-film fuel cells can achieve excellent performance at 800 °C and above, both electrolyte conductivity and electrode kinetics become limiting at lower temperatures. This is certainly the case for zirconia electrolytes and LSM based air electrodes (we have not observed the nickel cermet electrode to be limiting at reduced temperatures). At temperatures below 600 °C it is unlikely that stabilized zirconia electrolytes can be used at all, and alternative materials such as ceria or lanthanum gallate electrolytes are needed. In order to obtain acceptable electrode performance at temperatures significantly below 800 °C the LSM electrode must be replaced by a more active material. We have observed good performance for cobaltite pervoskite electrodes such as $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.98}\text{Ni}_{0.02}\text{O}_3$ (LSCN). Although the reactive nature of these materials precludes co-firing with YSZ electrolytes, excellent results have been obtained with ceria electrolytes.

Samaria and gadolinia doped ceria (CSO and CGO) electrolyte films were successfully deposited onto porous NiO-ceria substrates followed by co-firing of the bilayer and deposition of LSCN air electrodes. Thin-film NiO-CGO/CGO/LSCN and NiO-CSO/CSO/LSCN fuel cells were tested in $\text{H}_2\text{-H}_2\text{O/air}$ environments over a broad temperature range. In Figure 6 the open circuit potential for the thin-film ceria cells is shown as a function of temperature. Increasing electronic conductivity of the ceria electrolyte with increasing temperature is an issue for these electrolytes, however, for reduced temperature operation ceria based cells have several advantages including their stability against cobalt-based air electrodes that perform well at low temperature.

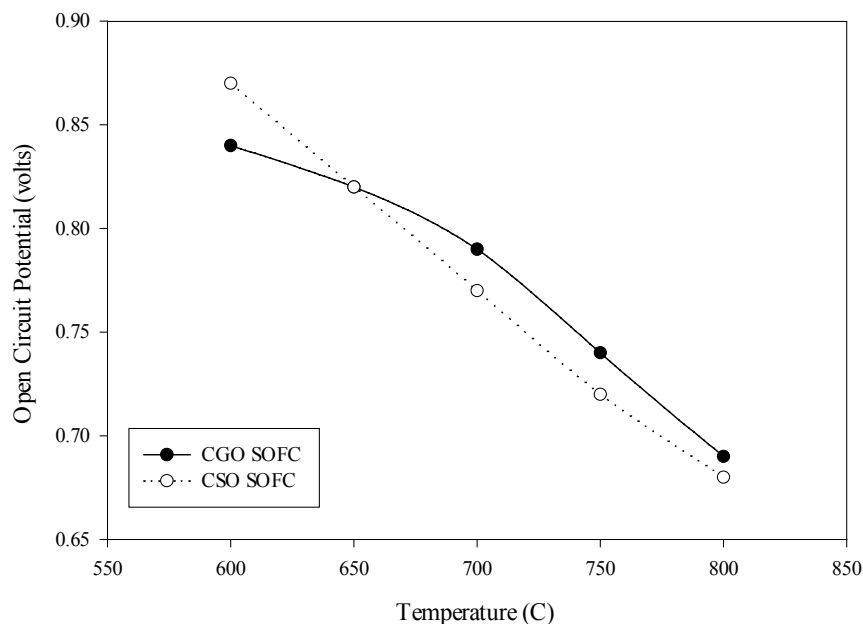


Figure 6. Open circuit potential vs. temperature for ceria based thin-film SOFCs.

As shown in Figure 7 the power density of thin-film ceria cells is not only high at temperatures between 650 °C and 750 °C, but up to current densities of 1000 mA/cm^2 , the **power density is almost invariant with temperature**. The insensitivity of cell power density to operating temperature is largely due to the inverse relationship of increasing electrolyte conductivity and electrode kinetics and decreasing cell potential with temperature. One can see from Figure 7 that at an **operating temperature of 650 °C** the ($\text{H}_2\text{-H}_2\text{O}$)NiO-CSO/CSO/LSCN(air) fuel cell attains a peak power density of over

500 mW/cm^2 . Even at temperatures as low as 600°C the CSO based cell attains a peak power density of 350 mW/cm^2 . Maximum power densities for both YSZ and CSO based thin-film cells are shown in Figure 8. At temperatures approaching 700°C and below the ceria based cells exhibit much better performance than that for YSZ electrolyte. Further optimization of the electrode materials and microstructure may lead to good SOFC performance at operating temperatures as low as 500°C , but this will be challenging.

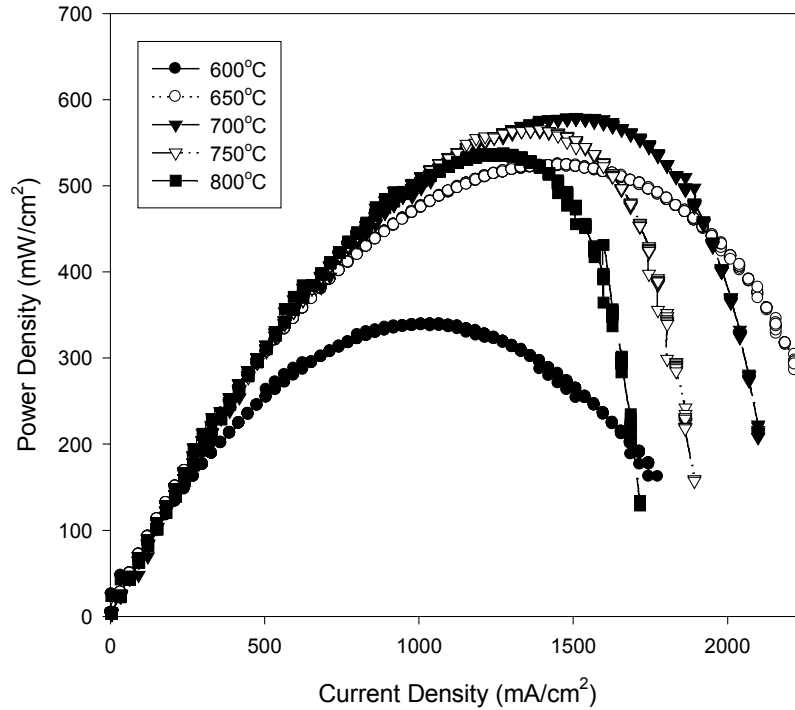


Figure 7. Power density of thin-film $(\text{H}_2\text{-H}_2\text{O})\text{NiO-CSO/CSO/LSCN(air)}$ SOFC.

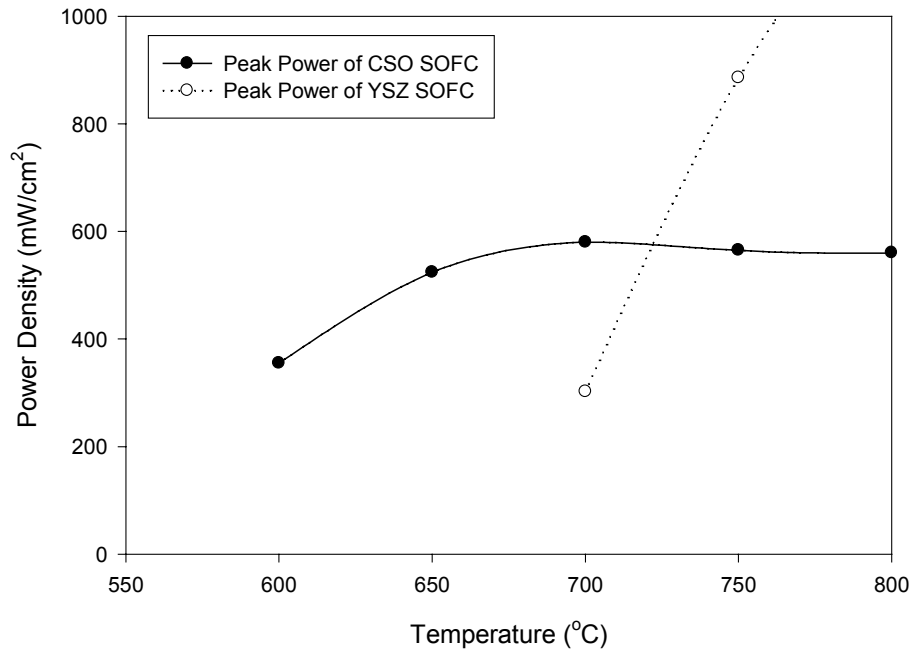


Figure 8. Peak Power vs. Temperature for YSZ and CSO based SOFCs.

Anode supported Proton Conductors

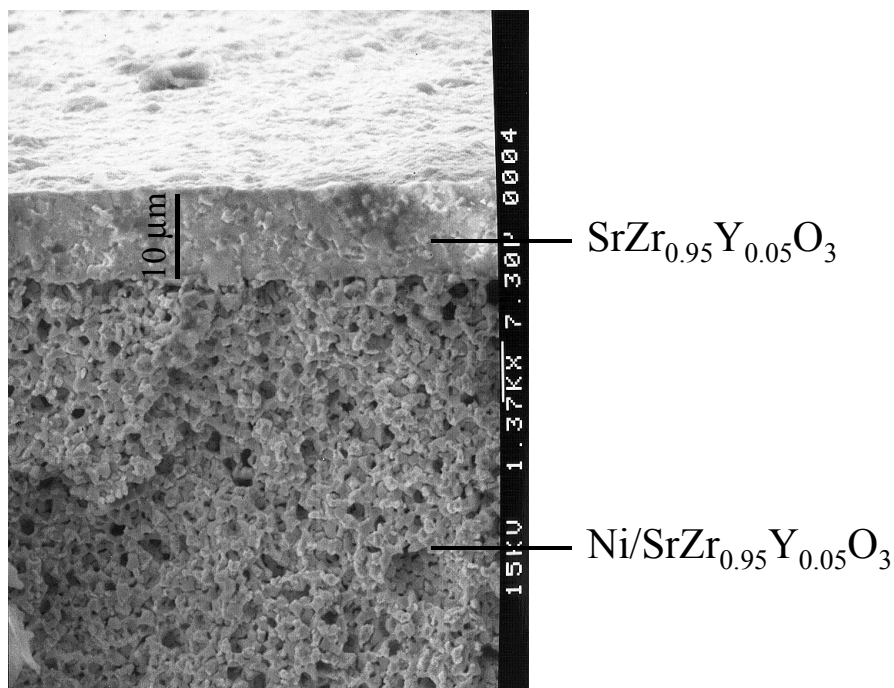


Figure 9. Co-fired strontium zirconate proton conducting thin-film on porous $\text{Ni/Sr}_{0.95}\text{Y}_{0.05}\text{O}_3$ cermet anode.

Cathode-supported Cells

For tubular cell designs having fuel supplied to the external surface of the cell tube, a cathode-supported structure is necessary. This is typically achieved using the electrochemical vapor deposition (EVD) process as used by Siemens Westinghouse Power Corporation (5). This type of structure can also be fabricated by colloidal deposition of a thin YSZ film onto a porous LSM substrate followed by co-firing of the bilayer structure. Particular care must be given to the sintering profile of the bilayer structure in order to avoid the formation of a resistive interface due to reaction of YSZ and LSM. Our group has been able to fabricate high quality YSZ films of 10 to 15 μm in thickness on porous LSM-YSZ substrates. In Figure 10 the current-voltage curve is shown for a symmetrical LSM-YSZ/YSZ/LSM-YSZ thin film cell operating in air; the cell is operating as an oxygen pump. Notably this cathode supported thin-film cell exhibits a very low overpotential of only 0.5 volts at a current density of 1500 mA/cm^2 . From the data in Figure 10 it is clear that cathode-supported thin-film cells can now be fabricated that rival the performance of anode-supported structures. Cathode-supported bilayers having nickel cermet anodes have also been fabricated and will be tested shortly in fuel cell environments.

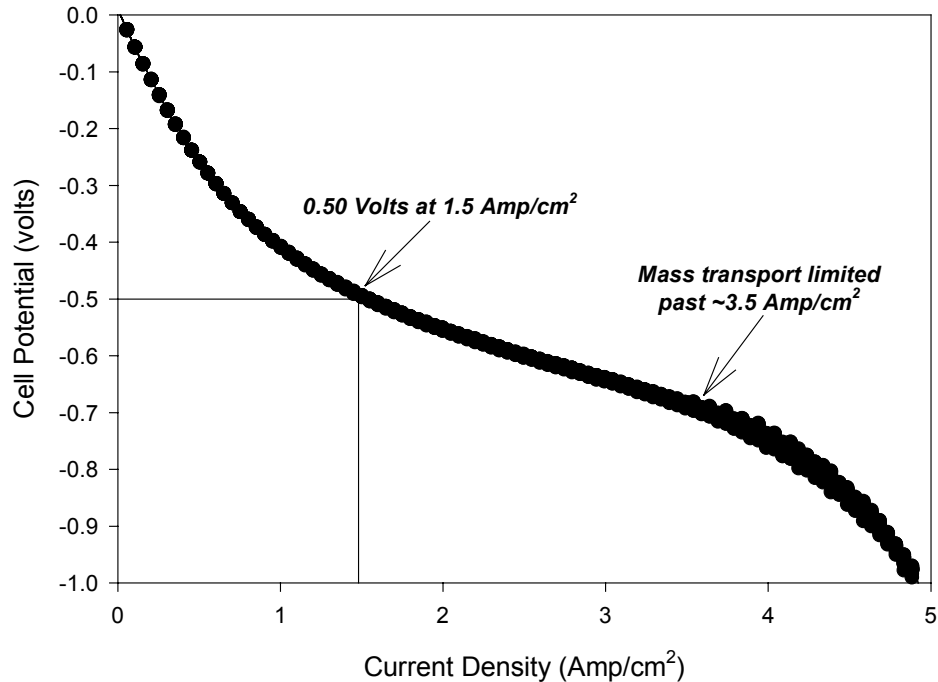


Figure 10. Current voltage relationship for a (air)LSM-YSZ/YSZ/LSM-YSZ(air) cell at 800 °C.

Tubular Cathode Supported Cells

In Figure 11 below, a co-fired cathode supported structure is shown. The microstructure and catalytic properties of the cathode is suitable for low temperature SOFC operation. The long-term stability of the structure is not yet known, but will be determined shortly. At operating temperatures of 800 °C or lower, sintering of the support structure is not anticipated to be a problem.

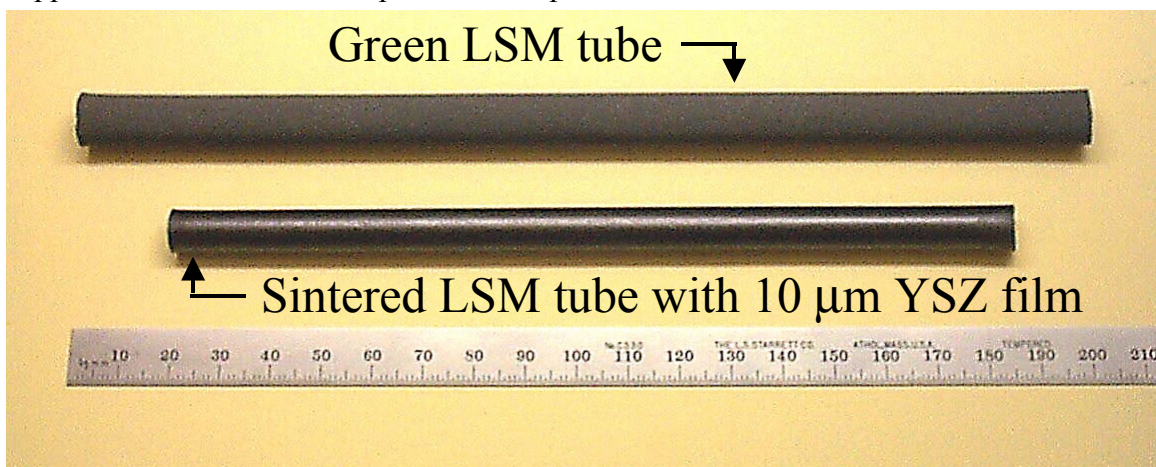


Figure 11. Porous LSM substrate co-fired with thin-film YSZ electrolyte to yield tubular cathode supported cell.

Cathode Supported Thin-Film Device by Constrained Sintering

Although the co-firing of electrode/electrolyte laminates is a reasonably straightforward method for producing thin-film electrolyte structures, there are situations where it is desirable to produce a thin-film electrolyte on a pre-fired substrate. Certainly, this approach can yield structures of remarkable dimensional stability, as is the case for the air electrode supported SOFC developed by Siemens-Westinghouse Power Corporation. However, densification of a colloidal deposit of electrolyte on a non-shrinking substrate introduces considerable complexity to sintering the film to full density. If successful, the colloidal approach can offer significant cost advantages over vapor deposition approaches. Siemens-Westinghouse, GRI and LBNL have been involved in collaborative research for several years addressing this problem. In Figure 12, a cross-section is shown of a thin YSZ film sintered onto a non-shrinking LSM air electrode. The film appears to be adherent and of high density.

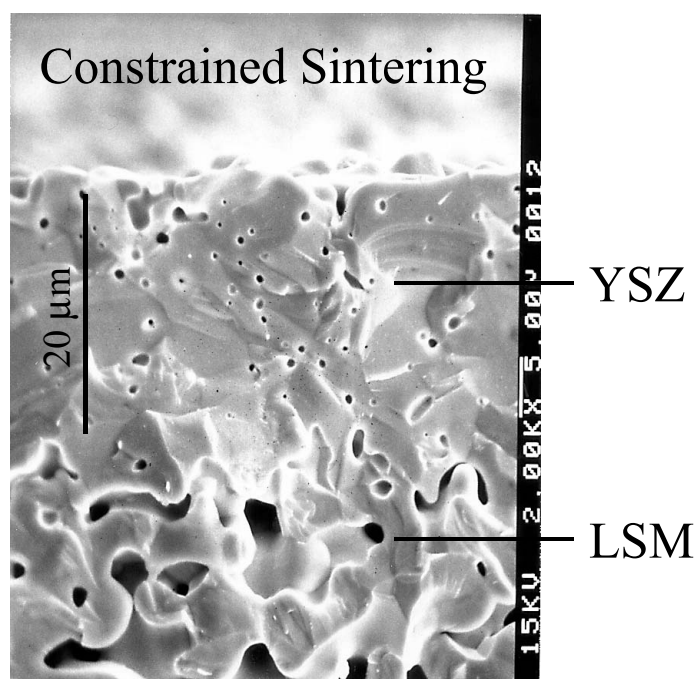


Figure 12. Porous non-sintering LSM substrate (supplied by Westinghouse) coated with YSZ electrolyte using colloidal techniques and densified under constrained sintering conditions.

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